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Spatial variability of soil chemical properties in Gazi Baba forest park region

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Abstract

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The soils in Gazi Baba forest park were examined. The field research was carried out in 2022, during which 22 surface soil samples were taken. In the framework of this master's thesis, an examination of some physical and chemical properties of the soil, as well as the content of the total forms of heavy metals, was carried out. Several soil types are formed in the area covered by the Gazi Baba forest park: regosols, cinnamon forest soils, colluvial soils, and complexes thereof. Based on the obtained values for the mechanical composition, for the most part, the soils in the surface part are sandy clay loam (SCL) at 41%, sandy loam (SL) at 36%, and loamy (L) soils at 23%. The content of total forms of heavy metals in all samples was analysed using atomic emission spectrometry with inductively coupled plasma (AEICP). The obtained results were processed statistically, and maps were made for the spatial distribution of all analysed elements and parameters. The obtained results allow us to distinguish between possible anthropogenic influences on the presence of heavy metals in the soils of Gazi Baba forest park and their lithological origin.

Keywords: physical-mechanical properties; characteristics; heavy metals

Introduction

The soil is a very specific component of the biosphere, because it is not only a geochemical pool to collect pollutants, but also acts as a natural buffer controlling the transport of chemical elements and substances to the atmosphere, hydrosphere and living organisms. Soil pollution by metals began with the anthropogenic smelting and processing of ore, which is confirmed by the investigation of snow and ice samples from Greenland (Boutron et al., 1995). Metals accumulated in the soil are extracted from soil by their dissolution, accumulation in plants, erosion or evaporation. However, the half-life is variable and depends on the element, ranging from a few decades to thousands of years (Ernst, 1998).

Urban pollution with heavy metals is a global problem initiated by the world's technological progress and human exploitation of natural resources, and as such has become the subject of many studies. The regional contamination of soil occurs mainly in industrial areas and within centres of large settlements, where factories, motor vehicles and municipal wastes are the most important sources of trace metals (Puteska et al., 2015; Petek et al., 2022).

Parks, city forests and public gardens are part of the city's green infrastructure. They provide all important ecosystem services, mitigate the effect of heat islands, contribute reduce air pollution, and provide a habitat for plant and animal species, but are and space for recreation for the city population (Larondelle and Lauf, 2016).

Regional soil contamination mainly occurs in industrial regions and centers with large populations, where the exhaust gases from motor vehicles and municipal waste are the main sources of traces of metals (Stafilov et al., 2017). Due to the heterogeneity and continuous change of the urban environment, it is first necessary to determine the natural distribution and methods for identifying anthropogenic anomalies in the natural environment. The natural background itself is variable, so higher concentrations of some elements may be normal in one area, but in another represent anomaly. Certainly there are cases when certain industry set beside, a city can increase soil pollution, and it is well known that extensive pollution in urban areas comes from industrial facilities (Mitkova et al., 2005, 2009; Pelivanoska et al., 2011; Krishna and Govil, 2005; Chen et al., 2005). The Gazi Baba forest park is an artificially raised forest, which from its formation until today, has become a real biocenosis with all its attributes. It is located in the center of Skopje, located on the hill of the same name. Due to its great importance, by decision of the city of Skopje, the forest is protected as a "characteristic landscape", and as such a protected area is under the authority of the city of Skopje, and it is managed by the public enterprise "Parks and Greenery". In 2015, the forest was declared a monument of nature.The total area of the characteristic landscape of Gazi Baba is 102.44 hectares. Several soil types are formed on this surface: regosols, cambisol, colluvial soils and complexes thereof. A large number of diverse deciduous and conifer species of trees and shrubs occur here, the most widespread being: black pine, ash, oak and others.Acknowledging the fact that the soils of city parks have a significant ecological regulatory role, the monitoring of such soils is exceptional is of importance. Many human recreational activities, different ground cover (trees, shrubs, bark, lawns) and road exposure, can divide the city park area into smaller fragments, different in their micro environmental conditions, which can contribute variability of soil chemical characteristics (Bonilla-Bedoya et al., 2021), therefore monitoring the quality of these soils is extremely important in order to preserve soil quality in city parks with timely measures.

Study area

The Skopje valley covers an area of 1924 km^2. The urban area covers an area of 225 km^2, with a width of 10 km (Vodno–Radišani), and in a length of 23 km (Dračevo–Gjorče Petrov) (Figure 1). The altitude in the centre of the city is 240 m. The region is clearly defined from the natural surroundings by mountain massifs. To the south the mountain of Jakupica separates it from the Pelagonia Valley, to the east the hill of Gradeški Rid separates it from Ovče Pole, to the north-east it is open to Kumanovo Valley, through the downhill near Romanovce, and to the north the mountain of Skopska Crna Gora separates it from the valley of Kosovo. The northern border region is also the state border with Kosovo. To the west the mountain of Žeden separates the Skopje Valley from the Polog Valley. The valley of the river of Vardar and its tributaries Treska, Lepenec and Pčinja, as well as the low folds to the neighboring valleys, allow the construction of road links and establishment of communications with neighboring environments (MOEPP, 2009; Stafilov et al., 2017) (Figure 1).

Fig. 1. Location of the investigated area in the Republic of North Macedonia

Figure 2 shows the map of the investigated area with the locations, where the soil samples were taken.

The region of Skopje is characterized by highly diverse and complex relief, which basically has the shape of a spacious valley and consists of high-brimmed edges and low central part. The relief of Skopje Valley has a predominantly tectonic character, and represents a deep tectonic furrow resulting from intensive and relatively young tectonic movements that are very little changed today. A number of genetic and chronological different elements participated in its creation, defined as pregravel elements, abrasion elements, characteristics of past lake conditions, fluvial elements and forms of glacial erosion (MOEPP, 2009).

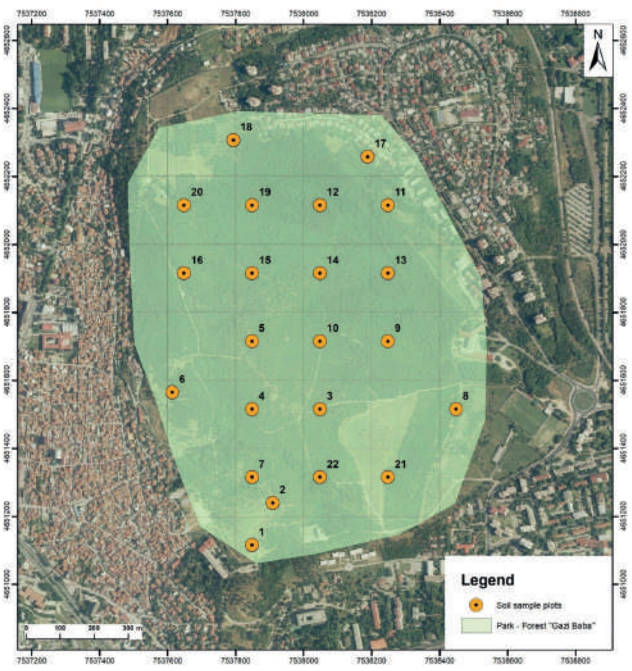


Fig. 2. Map of the investigated area with locations, where the soil samples were taken

Geographical location and orographic characteristics are the major modifiers of the climate in Skopje Valley. There is no direct influence of the Mediterranean climate, and it is directly affected by continental influences, while a typical mountain climate prevails in the higher mountains. Therefore, Skopje Valley is the final part of the country, in which the hot air currents along the Vardar river valley from the Aegean Sea could be present and as such it is a special region that feels the impact of local factors on the thermal regime (MOEPP, 2009). The valley of Skopje is built of Neogene and Quaternary sediments, and its mounts and hilly parts consist of rock masses of various ages. Precambrian rocks are present in the southern part of the valley in various petrographic varieties (gneiss, mica, leptinolites, cipolines and marbles). Magmatic granite rocks are embossed in these rocks in the spots, and today are quite changed (i.e. highly metamorphosed) (Pančevski et al., 2016; Markoski et al., 2023).

Today's appearance of the vegetation in the Gazi Baba nature park represents a combination of autochthonous and allochthonous species. The area is dominated by woody species, which are mostly planted with afforestation. Most of the trees are between 40 and 50 years old. The representation of different species of trees and shrubs has been investigated several times so far. According to the latest research, (MOEPP, 2009), 79 species of trees and shrubs found in this area have been determined. According to the data from the floristic literature, which has not been fully studied for this locality, at this moment in the Gazi Baba forest park, 141 plant species from 31 families can be listed, but their number is probably higher. Such an incomplete assessment of the state of the flora in this area nevertheless indicates that even here, in conditions of maximum human influence, a certain number of interesting autochthonous plant species have been preserved.

Material and Methods

Samples of surface soil (0–30 cm) were collected for analysis from 22 previously defined locations in the study area (Figure 2). All samples were collected in accordance with specific standards for collecting soil. Each sample must be representative, which means each sample should be a mixture of five samples, collected in an area of 10 × 10 m. It is important to collect the sample at each defined coordinate. The soil samples were packed in polyethylene bags, marked with a code and sample number. Samples pretreatment was done in accordance with ISO 11464:2006. First, they were air-dried, and after that crushed and sieved through a 2-mm sieve. Soil properties were determined, such as mechanical composition, pH (10390:2005), total nitrogen (11261:1995). The content of organic carbon and humus – Spectrophotometric determination with the dichromatic method, according to Walkley and Black, a validated method of the Faculty of Agricultural Sciences and Food in Skopje (Durdjević, 2014), and calcium carbonate equivalent volumetrically (ISO 10693). Additionally, total organic carbon (TOC) was determined by dry combustion (according to ISO standard 10694), extractable phosphorus and potassium (ammonium lactate method), while the cation exchange capacity (CEC) was measured by the method described by (Sumner and Miller, 1996).

The following elements were analyzed: Hg, Co, As, Li, Pb, Cd, Cr, Sn, Zn, Cu, Fe and Mn. Obtained content of As, Cd and Co were under the detection limits, and therefore, they are not presented. Soil samples were digested by two methods: Aqua Regia extraction method (ISO 11466) and digestion for determination the total element content with HF method (ISO 14869-1). Aqua regia (HCl and HNO_3 3+1) extraction method was done after digestion at 180ºC for 2 h. Soil samples (3.00 g) were digested directly in the relux digestion vessels, where 21 ml HCl and 7 ml HNO_3 were added. The solution was brought to boil and the relux was kept for 2 h. The solution of each vessel was quantitatively transferred to 100 ml lasks. For total digestion, soil samples (0.25 g) were placed in a Telon digestion vessel, and were digested on a hot plate. In the first step, HNO_3 was added to remove all organic matter, then a mixture of HF and $HClO_4$ was added, followed by a third step, where HCl and water were added to dissolve the residue. The solution was transferred quantitatively to the 25 ml volumetric lask. All reagents were of analytical grade (Merck, Germany). Analytical blanks were included in all extractions. Analysis of soil samples was performed using inductively coupled plasma-atomic emission spectrometry (ICP-AES). From the obtained results, descriptive statistics were prepared and multivariate factor analyses by R-method were applied, in order to identify the associations of the chemical elements (Reimann et al., 2002). Spatial distribution maps were prepared for each factor using universal kriging method with a linear variogram interpolation. Factor analysis is the methodological basis of a set of statistical techniques, used to analyse inter-relations of many variables. The approach includes processing information from a large number of original variables into smaller sets (called factors) with minimal loss of information from the original variables. Factor analysis, as a set of statistical and mathematical procedures, is useful in investigations whereby a number of variables that are mutually correlated, and where is necessary to determine the basic source of covariance between the data (Reimann et al., 2002). Multivariate cluster analysis was also applied to determine the significance of the factor analysis and the stability of the new synthetic variables, that is, associations of elements. The dendrogram of the distances among the individual elements is presented in Figure 3. Identical results were achieved by application of multivariate factor analysis. All of the obtained clusters correspond to the four obtained factors.

Results and Discussion

According to the obtained data, the soils in the surface part have a heterogeneous mechanical composition. The mechanical composition has an influence on the availability of heavy metals. At the same total content, the availability and mobility of heavy metals is higher in soils with a lighter mechanical composition (sandy), compared to heavier soils (clay). This means that the danger of translocation (moving) of heavy metals to groundwater and their pollution, with all the negative consequences for the ecosystem, is greater in soils with a lighter mechanical composition.

From the analyzed soil samples (Table 1), it can be seen that the fraction of total sand is dominated by the fraction of fine sand, on average 39.02% in relation to coarse sand 8.98%. The average value of the physical sand fraction (fine + coarse sand) is 48.00%, and is lower than the physical clay fraction (clay + silt), which is 52.00%. The median for the total sand fraction is 50.35%. In the physical clay fraction, the clay fraction with the highest average value is 27.19%, and ranges from 11.70 to 51.60% in relation to the powder fraction, which averages 24.80%. The median for the powder fraction is 25.20% higher than the median for the clay fraction – 23.05%.

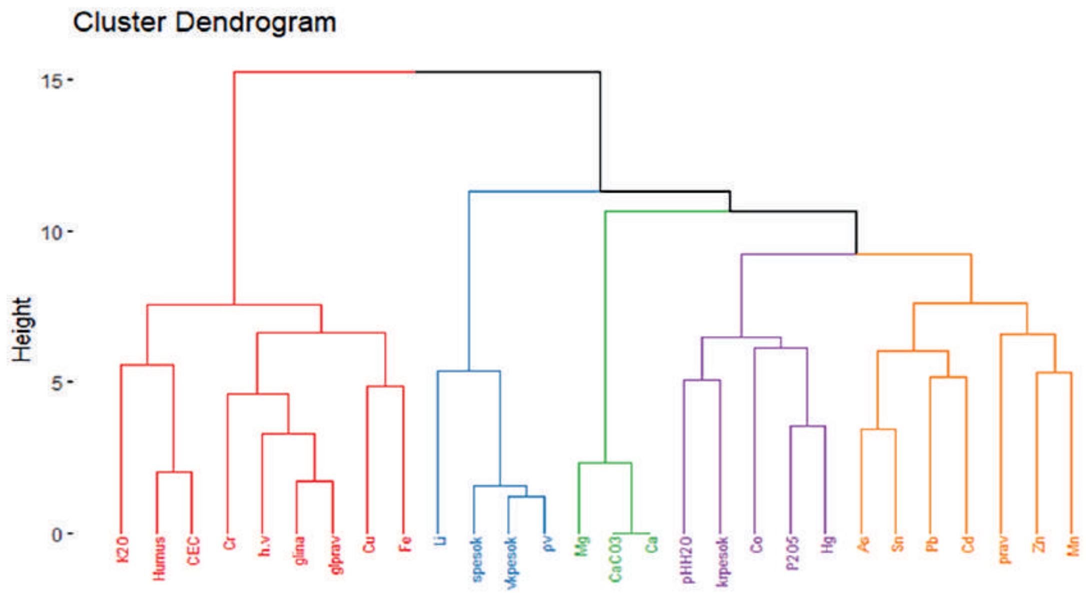


Fig. 3. Dendrogram from the cluster analysis of the soil samples

Table 1. Descriptive statistics for the content of the analyzed elements in the soil samples

Parameters	Measurement values	n	min	max	X	SD	Md
pH in H_2O	/	22	7.58	8.81	8.45	0.34	8.61
$CaCO_3$	[%]	22	7.91	23.32	13.2	4.17	11.87
Humus	[%]	22	1.94	16.6	4.08	3.2	3.11
P_2O_5	[mg/100 g soil]	22	4.31	48.94	13.26	8.99	10.83
K_2O	[mg/100 g soil]	22	34.76	72.13	53.77	12.34	52.11
CEC	[cmol(+) kg^{-1}]	22	13.15	59.38	21.74	10.4	17.67
Hygroscopic moisture	[%]	22	1.17	4.17	2.52	1.08	2.39
Coarse sand	[%]	22	4.14	19.63	8.98	3.84	7.98
Fine sand	[%]	22	19.63	64.11	39.02	12.08	42.23
Total sand	[%]	22	25.1	71.4	48	13	50.35
Silt	[%]	22	10	32.5	24.8	4.91	25.2
Clay	[%]	22	11.7	51.6	27.19	13.13	23.05
Clay + Silt	[%]	22	28.6	74.9	52	13	49.65
$\boldsymbol{\rho_p}$	[g/cm^3]	22	1.24	1.54	1.39	0.09	1.41
Ca	[%]	22	3.16	9.32	5.28	1.67	4.75
Mg	[%]	22	1.12	4.16	2.28	0.76	2.1
As	[mg/kg]	22	0.035	0.779	0.22	0.18	0.16
Co	[mg/kg]	22	0.783	6.706	4.54	2.08	5.52
Cd	[mg/kg]	22	0.019	0.886	0.3	0.24	0.24
Cr	[mg/kg]	22	30.85	108.44	69.79	23.55	68.88
Cu	[mg/kg]	22	30.16	65	39.82	8.01	38.71
Fe	[%]	22	2.36	4.18	3.37	0.55	3.31
Hg	[mg/kg]	22	0.0011	0.043	0.01	0.01	0.008
Li	[mg/kg]	22	0.106	0.277	0.15	0.05	0.144
Mn	[mg/kg]	22	610	860	700	100.0	710
Pb	[mg/kg]	22	26.69	34.87	30.25	2.48	29.87
Zn	[mg/kg]	22	67.15	105.75	82.5	10.83	81.89
Sn	[mg/kg]	22	0.0076	1.655	0.17	0.36	0.062

(n = 22)

The soil samples according to the American classification triangle, with the obtained values for the mechanical composition, are classified into textural classes (Mitkova and Markoski, 2022). Based on the obtained values, for the most part the soils in the surface part are sandy clay loam (SCL) 41%, then sandy loam (SL) − 36% and 23% are loamy (L) soils.

Table 2 presents the factor analysis, that is, the loading matrix of dominant rotating factors. With factor analysis, a small number of synthetic variables called factors are obtained from a large number of variables. The factors contain meaningful information about the original variables, and have a precisely determined meaning. Factor analysis was performed on variables standardized to zero and unit standard deviation (Reiman et al., 2002).

Five principal components (PC) were identified, with Eigen-value > 1, which explained 68.09 % of the total variability. PC 1 explains 28.52 % of the total variability, which is due to the high correlation of humus, K_2O, CEC, hygroscopic moisture, clay, clay + silt, Cr, Cu and Fe with this RS. The highest negative correlation with PC 1 was observed for fine sand, total sand, ρp and Li. $CaCO_3$, Ca, Mg and dust have the largest share in the second main component, and Hg is negatively correlated with PC2. The biggest variability of PC 3 is explained by coarse sand, Co, As, Pb, Sn, Zn and Mg. Humus and Cd participate in PC 4, and the highest negative correlation with pH-H_2O was found. P_2O_5 has the highest positive correlation with PC 5.

In the first cluster are grouped K_2O, humus, CEC, Cr, hygroscopic moisture, clay, clay + dust, Cu and Fe, properties with the highest positive correlation with PC 1. In the second cluster are fine sand, total sand, ρp and Li, which have the highest negative correlation with RS1. In the third cluster are grouped $CaCO_3$, Ca and Mg, in the fourth pH-H_2O, coarse

Table 2. Loading matrix of dominant rotating factors

Parameters	PC1	PC2	PC3	PC4	PC5
pH in H_2O	0.144	-0.44	0.054	-0.481	-0.221
$CaCO_3$	-0.162	0.771	0.309	-0.42	0.191
Humus	0.406	0.208	-0.076	0.521	0.185
P_2O_5	-0.088	-0.482	0.255	-0.056	0.711
K_2O	0.515	0.074	-0.223	0.307	0.447
CEC	0.736	0.245	-0.08	0.367	0.094
Hygroscopic moisture	0.835	-0.08	0.176	0.368	0.094
Coarse sand	-0.277	-0.473	0.568	-0.348	-0.077
Fine sand	-0.893	-0.16	-0.167	0.149	0.049
Total sand	-0.911	-0.288	0.012	0.036	0.023
Silt	-0.12	0.394	-0.022	0.089	0.279
Clay	0.946	0.139	-0.003	-0.069	-0.126
Clay + Silt	0.911	0.289	-0.012	-0.036	-0.023
ρ_p	-0.955	-0.173	-0.011	0.071	0.103
Ca	-0.163	0.772	0.309	-0.42	0.189
Mg	-0.113	0.799	0.195	-0.381	0.138
Hg	0.12	-0.609	0.455	-0.086	0.43
Co	0.171	-0.128	0.485	0.116	0.006
As	-0.389	0.104	0.555	0.085	-0.415
Li	-0.655	0.302	-0.318	-0.032	0.174
Pb	-0.243	0.371	0.559	0.338	0.214
Cd	0.205	0.079	0.536	0.588	-0.096
Cr	0.707	-0.215	0.331	-0.059	-0.144
Sn	-0.333	0.128	0.452	0.367	-0.456
Zn	0.09	-0.248	0.494	0.083	0.16
Cu	0.42	-0.201	-0.395	-0.113	-0.099
Fe	0.513	-0.505	0.076	-0.134	0.256
Mn	0.283	0.151	0.387	-0.024	0.044
Eigen-value	7.98	4.07	3.06	2.16	1.79
% variability	28.52	14.52	10.94	7.73	6.38
% cumulative variance	28.52	43.04	53.98	61.71	68.09

sand, Co, P_2O_5 and Hg, and in the fifth cluster all other examined properties (As, Pb, Sn, Cd, dust, Zn and Mg).

The results obtained from the investigations of the chemical properties of the soil samples are presented in Table 1. The comparison of the obtained results Table 3 (the median, minimum and maximum value of the contents of heavy metals in the soil samples from the region of Gazi Baba, with those from the entire territory of the Republic of North Macedonia, (Stafilov and Šajn, 2017), the territory of Skopje (Stafilov et al., 2017) and in Europe (Salminen et al., 2005).

The soil samples are carbonate. The average value for all soil samples is 13.20% (minimum 7.91% and maximum 23.32%), and the median is 11.87%. The values for the reaction of the soil solution are very significant, because the solubility and insolubility of heavy metals in the soil depends on them, that is, their availability or unavailability in the soil.

According to Mitkova et al. (2009), the uptake of a large number of heavy metals is enhanced by increasing acidity. In the examined soil samples, the reaction of the soil solution in water ranges from 7.58 to 8.81, the average is 8.45 (weakly to strongly alkaline, according to the US classification), and the median is 8.61. These values indicate a reduced availability of heavy metals in the soil. The adsorption capacity ranges from 13.15 to 59.38 cmol/kg^{-1}, mean 21.74 cmol/kg^{-1}, or with a median of 17.67 cmol/kg^{-1}. The contents of readily available forms of P_2O_5 and K_2O range from 4.31 mg/100 g soil to 48.94 mg/100 g soil for phosphorus, with a median of 10.83 mg/100 g soil. The potassium content is higher. That ranges

Table 3. Comparative analysis of the median, minimum and maximum value of the content of elements in soil samples from the region of Gazi Baba, Skopje, North Macedonia and Europe

Element	Value	Gazi Baba		Skopje (Stafilov et al., 2017)		North Macedonia (Stafilov & Sajn, 2016)		Europa (Salminen et al., 2005)	
		Md	min-max	Md	min-max	Md	min-max	Md	min-max
As	mg/kg	0.164	0.035 – 0.779	12	0.05 − 68	10	1.0 − 720	12	0.32 − 562
Co	mg/kg	5.52	0.783 – 6.706	38	0.12 − 130	17	0.50 − 150	8	< 1.0 − 191
Cd	mg/kg	0.24	0.019 – 0.886	4.9	0.005 − 12	0.30	0.01 − 110	0.92	0.030 − 14
Cr	mg/kg	68.88	30.85 – 108.44	100	42 − 350	88	5.0 – 2 700	60	< 3 − 6 230
Cu	mg/kg	38.71	30.16 – 65.00	33	7.3 − 590	16	1.7 − 73	13	0.81 − 256
Fe	%	3.31	2.36 – 4.18	3.1	1.1 – 5.2	2.5	0.63 – 6.7	2.46	1.12 – 15.6
Hg	mg/kg	0.008	0.0011 – 0.043	0.13	0.005 – 6.1	–	–	0.037	0.005 – 1.35
Li	mg/kg	0.144	0.106 – 0.277	–	–	18	4.8 − 79	–	–
Mn	mg/kg	710	610 − 860	720	340 − 5 600	620	160 − 3 200	507	31 − 6 068
Pb	mg/kg	29.87	26.69 – 34.87	51	5.0 − 290	17	2.5 − 700	10	5.32 − 970
Zn	mg/kg	81.89	67.15 – 105.75	100	23.0 − 18 000	39	3.1 − 440	52	< 3 − 2 900
Sn	mg/kg	0.062	0.0076 – 1.655	4.8	0.005 − 150	2.6	< 0.10 − 680	3	< 2.0 − 106

from 34.76 to 72.13 mg/100 g soil, with a median of 52.11 mg/100 g soil. The mean value of Ca is 5.19%, which means that the soil samples are very highly supplied with calcium. The median for Ca content is 4.75%. The content of magnesium is from 1.12 to 4.16%, medium 2.28% (highly supplied). The median for Mg is 2.10%. The average value of arsenic content in the soils of the examined area of the Gazi Baba forest park is 0.22 mg/kg (the lowest value is 0.035 mg/kg, and the highest is 0.78 mg/kg). The median for the arsenic content in the samples is 0.164 mg/kg. The minimum value of cobalt in the Gazi Baba forest park is 0.783 mg/kg and is higher than the minimum cobalt content for the wider territory of Skopje, which is 0.12 mg/kg and for North Macedonia – 0.50 mg/kg.

However, this lowest value of cobalt is within the European minimum values, which amount to < 1.0 mg/kg. The highest value of cobalt in the Gazi Baba forest park is 6.71 mg/kg, which is much lower than the values obtained for the wide area for Skopje (130 mg/kg) and for North Macedonia (150 mg/kg), and much lower than Europe (190 mg/kg). The median for cobalt is 5.52 mg/kg, and is lower than the medians for Skopje (38 mg/kg), for North Macedonia (17 mg/kg) and for Europe (8.0 mg/kg). The average value of the cadmium content is 0.30 mg/kg, the lowest value is 0.02 mg/kg, and the highest is 0.89 mg/kg. The obtained minimum value of cadmium in the Gazi Baba forest park is higher than the minimum cadmium content for the wider territory of Skopje (0.005 mg/kg) and for North Macedonia (0.01 mg/kg), probably due to the pollution from the steel plant, located in close proximity to the Gazi Baba forest park. However, this lowest value is within the European minimum values for cadmium, which are < 1.0 mg/kg. The median of the cadmium content in this area is 0.24 mg/kg, and is lower than the median of cadmium for the territory of Skopje (4.9 mg/kg), and is closer to the median in the soil samples of the territory of North Macedonia (0.30 mg/kg). Retention of cadmium in soil is correlated with humus content (higher adsorption capacity). According to Kastori (1997), the increased content of humus in the surface horizon contributes to the increased adsorption of cadmium in the surface soil layer. Content humus of the soils formed upon limestones and dolomites varies extensively, and depends on the deposition of nearby materials (from the higher places), and on the degree of erosion, altitude, vegetation, relief, evolution and the intensity of the soil forming process (Markoski et al., 2015). Andreevski et al. (2010) and Kastori (1997) pointed out that soils containing $CaCO_3$ bind cadmium well, and reduce its availability to plants and microorganisms. The examined soil samples have a high content of $CaCO_3$. Considering that the content of total cadmium in all soil samples is lower than the reference values, and the present carbonates affect or reduce its availability, this means that there is no danger of soil contamination and phytotoxic effect.

The content of chromium in the area of the Gazi Baba forest park averages 69.79 mg/kg, the lowest value is 30.85 mg/kg, and the highest is 108.44 mg/kg. It can be noted that its minimum value is much higher than the minimum value for the entire territory of North Macedonia (5.0 mg/kg), and for Europe < 3.0 mg/kg, and lower compared to the territory of Skopje, 42 .0 mg/kg. Its highest values in the soil samples from the researched area are lower than the values, obtained for the territory of Skopje, 350 mg/kg, for North Macedonia, 2 700 mg/kg and for Europe, 6230 mg/kg. The median content of chromium in soil samples is 68.88 mg/kg, and if compared to the soils in North Macedonia and the territory of Skopje, it is lower and higher compared to the median for soils in Europe, 60.0 mg/kg kg.

The values for the copper content in the soil samples range from 30.16 mg/kg to 65.00 mg/kg, average – 39.82 mg/kg. The obtained minimum values of copper for the area of the Gazi Baba forest park are higher than the obtained values for the investigated soils for the territory of Skopje

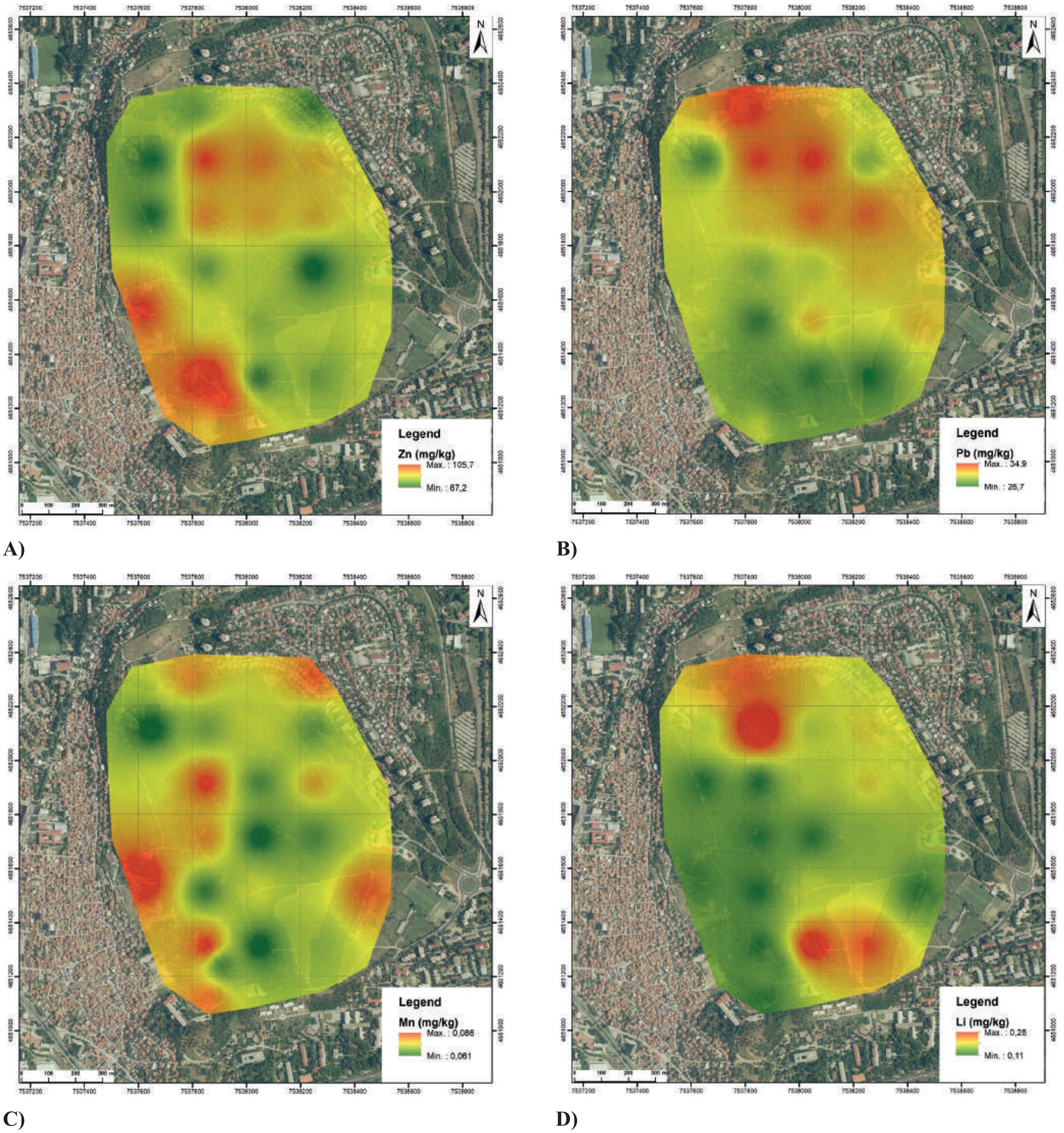
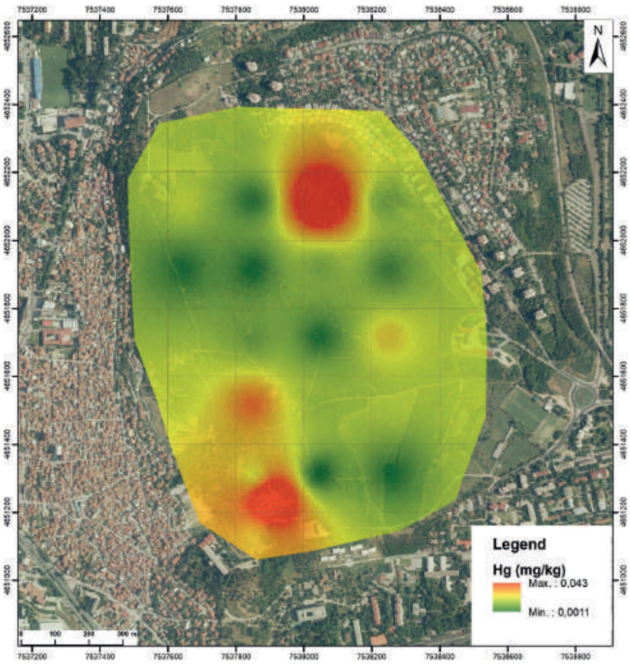
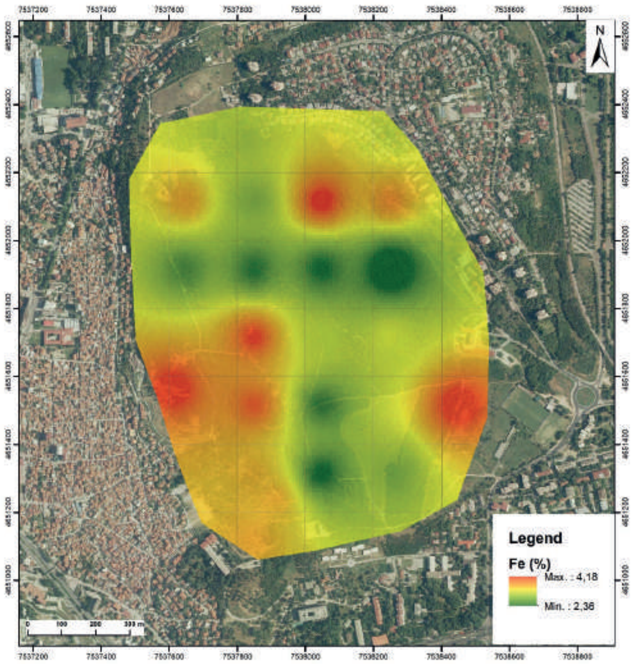


Fig. 4. Spatial distribution of the researched elements area in the Gazi Baba Forest Park

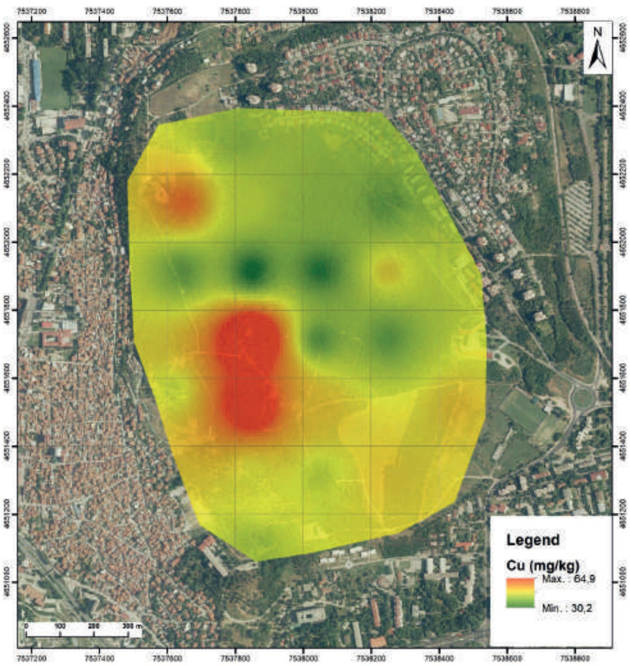
(7.3 mg/kg), for the North f Macedonia (1.7 mg/kg) and for the soils in Europe, 0.81 mg/kg. The highest values of copper for the area of the Gazi Baba forest park are lower than those for the territory of Skopje (590.0 mg/kg), for North Macedonia (73.0 mg/kg) and for Europe, 256.0 mg/kg. The median copper content in the examined soil samples is 38.71 mg/kg, and is higher compared to the soils of North Macedonia (16.00 mg/kg), for the territory of Skopje (33.0 mg/kg), and



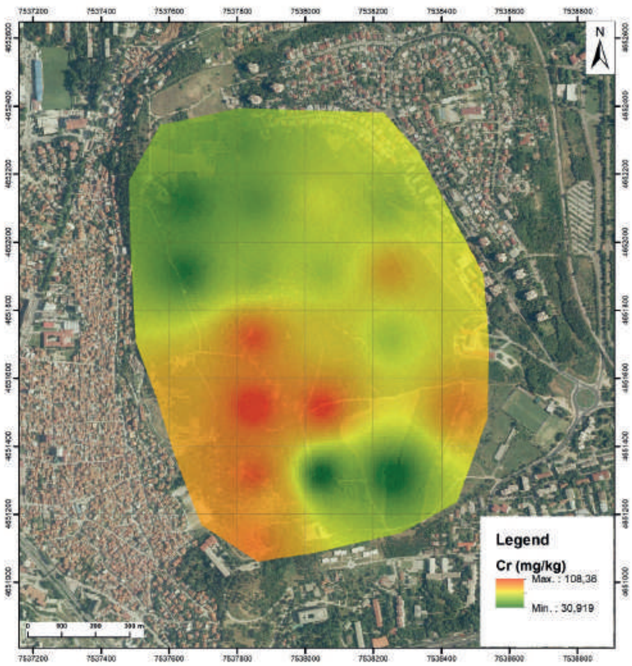
E)



F)



G)



H)

Fig. 4. Continued

for Europe (13 mg/kg) Figure. 4. (A; B; C; D; E; F; G; H; I; J; K; L).

The values for the Fe content in the soil samples range from 2.36% to 4.16%, with a median of 3.31%. The mean value of the mercury content in the soils of the investigated area of the Gazi Baba forest park is 0.0103 mg/kg. The lowest value is 0.0011 mg/kg, and the highest is 0.043 mg/kg. The median for the mercury content in soils is 0.008 mg/kg,

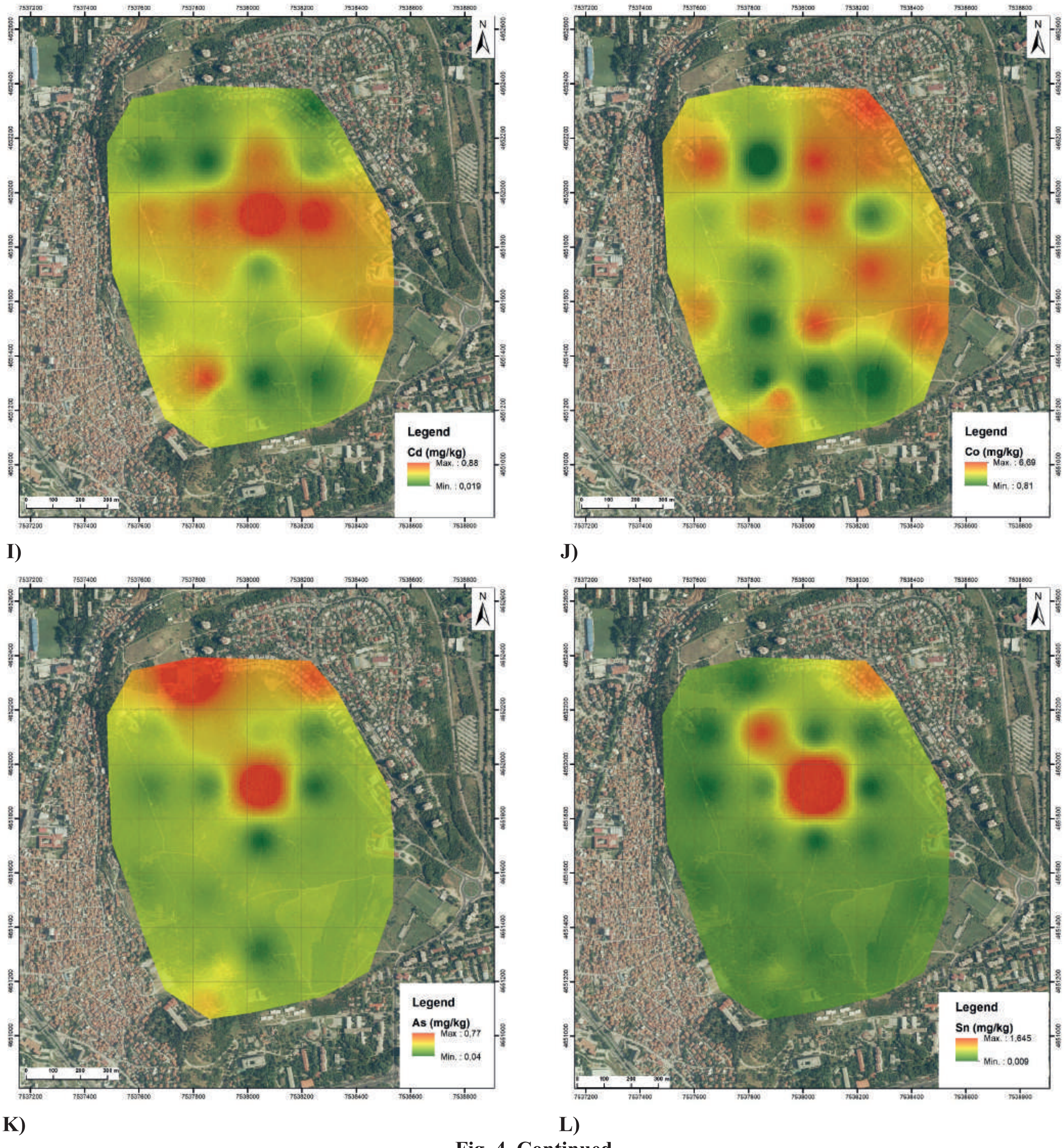


Fig. 4. Continued

and is much lower compared to the median values for soils from the territory of Skopje (0.13 mg/kg) and for Europe (0.037 mg/kg). Mercury content in the examined soil samples from the Gazi Baba forest park is much lower than the intervention value.

Lithium in the researched area of the Gazi Baba forest park ranges from 0.106 mg/kg to 0.277 mg/kg, the average is 0.148 mg/kg, and the median is 0.144 mg/kg.

Manganese has an almost twice higher minimum value (610.0 mg/kg) compared to the minimum value of manganese for the territory of Skopje (340 mg/kg), as well as in the surface part of the soils in RS Macedonia (160.0 mg/kg). The minimum value of manganese is higher than the minimum value in the surface part of the soils in Europe (31.0 mg/kg). The highest value of manganese in the examined soil samples (860 mg/kg) is lower, compared to all the highest values for the territory of Skopje (5600 mg/kg), for the North Macedonia (3 200 mg/kg) and for Europe, which is 6068 mg/kg. The median for the manganese content in the soil samples is 710 mg/kg, which correlates with the lowest, highest and middle values for this element and is similar to the median for the territory of Skopje (720 mg/kg), and is higher than the median for Europe (507 mg/kg).

Values for lead content in soil samples range from 26.69 mg/kg to 34.87 mg/kg, with a median of 27.87 mg/kg. These values are the result of lithogenic origin and anthropogenic origin: by the Ironworks and other industrial facilities, that are in the immediate vicinity, as well as by exhaust gases from cars. The obtained minimum values of lead for the area of the Gazi Baba forest park are higher than the obtained values for the investigated soils for the territory of Skopje (5.0 mg/kg), for the North Macedonia (2.5 mg/kg), and for the soils in Europe (5.32 mg/kg). Compared to the lowest, the highest values in the Gazi Baba forest park are lower, compared to those from the territory of Skopje (290.0 mg/kg), from North Macedonia (700 mg/kg), and from Europe (970 mg/kg). The median of 27.87 mg/kg is higher than the median for North Macedonia (17.0 mg/kg) and for Europe (10.0 mg/kg), and is lower than the median for the territory of Skopje, 51.0 mg/ kg.

The content of total lead is much lower than the reference values in all soil samples, which means that the natural background is low and anthropogenic contamination is negligible or absent. This indicates that there is no danger of contamination of plants with this heavy metal.

The average value of the zinc content in the soils of the studied area of Gazi Baba is 82.50 mg/kg, the lowest is 67.15 mg/kg, and the highest is 105.75 mg/kg. The lowest value in the Gazi Baba forest park is almost three times higher, compared to the lowest value from the wide area of the Skopje region (23.0 mg/kg), and much higher than the lowest value in the surface part of the soils in North Macedonia (3.1 mg/kg), and for Europe (below 3.0 mg/kg). Higher zinc content in the industrial zone is mainly due to dust pollution from the steel mill.

The average value of the content of selenium in the soil samples from the investigated area of Gazi Baba is 0.17 mg/kg, the lowest is 0.0076 mg/kg, and the highest is 1.655 mg/kg. The median is 0.062 mg/kg and this value is lower than the median for the region of Skopje (4.8 mg/kg), for North Macedonia (2.6 mg/kg), and for Europe (3.0 mg/kg).

Conclusion

Based on the obtained results for the spatial distribution of heavy metals in the soils of the researched area in the Gazi Forest park Grandma, the following conclusions can be drawn: On the area covered by the Gazi Baba forest park, several have been formed soil types: regosols, cinnamon forest soils, colluvial soils and complexes thereof.

Five principal components (PC) were identified, with Eigen-value > 1, which explained 68.09 % of the total variability. PC 1 explains 28.52 % of the total variability, which is due to the high correlation of humus, K_2O, CEC, hygroscopic moisture, clay, clay + silt, Cr, Cu and Fe with this RS. The highest negative correlation with PC 1 was observed for fine sand, total sand, ρp and Li. $CaCO_3$, Ca, Mg and dust have the largest share in the second main component, and Hg is negatively correlated with PC2. The biggest variability of PC 3 is explained by coarse sand, Co, As, Pb, Sn, Zn and Mg. Humus and Cd participate in PC 4, and the highest negative correlation with pH-H_2O was found. P_2O_5 has the highest positive correlation with PC 5.

In the first cluster are grouped K_2O, humus, CEC, Cr, hygroscopic moisture, clay, clay + dust, Cu and Fe, properties with the highest positive correlation with PC 1. In the second cluster are fine sand, total sand, ρp and Li, which have the highest negative correlation with RS1. In the third cluster are grouped $CaCO_3$, Ca and Mg, in the fourth pH-H_2O, coarse sand, Co, P_2O_5 and Hg, and in the fifth cluster all other examined properties (As, Pb, Sn, Cd, dust, Zn and Mg).

The reaction of the soil solution in water ranges from 7.58 to 8.81, the mean is 8.45 (weakly to strongly alkaline, according to the US classification), and the median is 8.61.

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